Integration of Photocurable Polymer Membranes with Ionophores for Multi-Ion LAPS

修士学位論文要約（令和２年３月）

マルチイオン LAPS 用のイオノフォアを含む光硬化性高分子膜の集積化

サイダ タハリマ
指導教員：吉信 達夫,　研究指導教員：宮本 浩一郎

Integration of Photocurable Polymer Membranes with Ionophores for Multi-Ion LAPS

Saida TAHARIMA
Supervisor: Tatsuo YOSHINOBU,　Research Advisor: Ko-ichiro MIYAMOTO

A light-addressable potentiometric sensor (LAPS) for multi-ion sensing has been developed by integrating photocurable ion-selective membranes, allowing simultaneous determination of two kinds of ions, K^+ and Na^+. Sensitivities to K^+ and Na^+ ions were characterized over a concentration range of 10^{-5} to 10^{-1} mol/l. A checker pattern of nine ion-selective membranes, four K^+ ion-selective membranes, and five Na^+ ion-selective membranes were fabricated on a single sensor chip and their sensitivities and cross-sensitivities were studied.

1. Introduction

In the (bio-) chemical field, determination of the composition of a sample solution is important. By combining transducers with different enzymes, cells or ion-selective membranes, various analytes can be measured. One example of such sensor is LAPS, a semiconductor-based potentiometric sensor that allows the determination of analyte concentrations in aqueous solutions in a spatially-resolved manner[1]. The advantage of the LAPS technique is that an arbitrary position on the sensing surface can be independently accessed with a light probe, e.g., a scanning laser beam. This "light-addressability" facilitates its application to an integrated multi-LAPS, in which different parts of the sensing surface are modified with different sensing materials such as ionophores[2] and enzymes. Ionophores are molecules that can selectively bind to a specific ion. By modifying the sensing surface with a plurality of membranes including different ionophores, a multi-ion-selective LAPS can be realized.

2. Chemicals

Valinomycin and sodium ionophore X were used for fabricating K^+ and Na^+ ion-selective membranes, respectively. Chlorotrimethylsilane, hexane, diheptyl phthalate (DHP) as plasticizer, glycidyl methacrylate (GM) as polymer matrix, 1,6-hexanediol diacrylate (HDODA) as cross-linker, potassium tetrakis (p-chlorophenyl)borate (K-TpClPB) as lipophilic additive, Benzoin methyl ether (BME) as photoinitiator were used. The aqueous solutions were prepared with deionized water.

3. Sensor fabrication

Four potassium ion-selective membranes and five sodium ion-selective membranes were fabricated on a single sensor chip to fabricate a multi-ion-selective LAPS. Prior to the fabrication of membranes, a partition made of SU-8 was prepared by a photolithographic process to define windows, in which the membrane cocktail was poured.

To improve the adhesion of membranes, silanization of the sensor surface was necessary by means of chlorotrimethylsilane. The treatment was carried out with 5 to 10% chlorotrimethylsilane in hexane at 55°C for 5 h, causing the substitution of the Si-OH surface groups with $Si\text{-}O\text{-}Si(\text{-}R)_3$ by a reaction:

$$Si\text{-}OH + R_3SiCl \longrightarrow Si\text{-}O\text{-}Si(\text{-}R)_3 + HCl$$

Later on, 2 μl of membrane cocktail was poured into each partition on the sensor surface and exposed to UV from a super high-pressure mercury lamp (USH-250D, Ushio) with a power of 250 W and a wavelength of 365 nm for 160 s.

4. Measurement setup

A 3 × 3 IR-LED array was used as a light source to illuminate the backside of the sensor surface and measurements were carried out simultaneously for each membrane. The illumination area of a single LED (measurement spot) was a circle of about 2.5 mm in diameter. Out of the sensing area of 18 mm × 18 mm on a sensor chip, an area of 14 mm × 14 mm was in contact with the electrolyte solution, in which an Ag/AgCl reference electrode was immersed. A preamplifier with an amplification factor of 10^6 VA^{-1} was used to amplify the photocurrent, which was then measured at a sampling rate of 10^5 samples/s. The schematic of the multi-ion LAPS system is depicted in Figure 1.

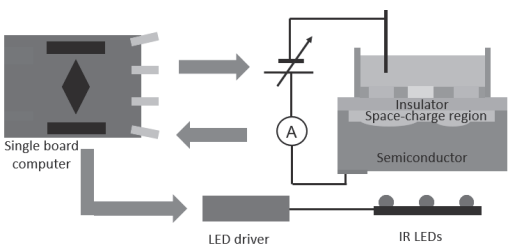

Figure 1: Multi-ion LAPS setup.

5. Results and Discussion

The characteristics of the ion-selective membranes were studied by measuring the I/V curves. The average of the bias voltage corresponding to the inflection points of the I/V curves at all measurement spots is plotted as a function of KCl and NaCl concentrations for K^+ and Na^+ ion-selective membranes as shown in Figure 2 and Figure 3, respectively. The sensitivity was determined by linear regression of the slope.

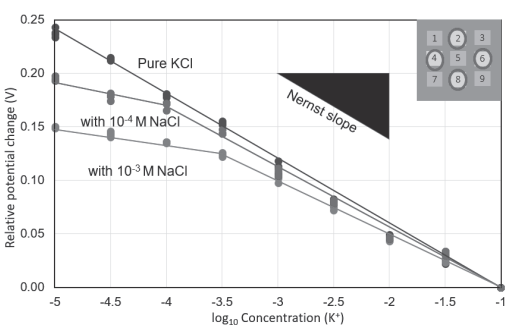

Figure 2: Calibration plot for the K^+ ion-selective membranes.

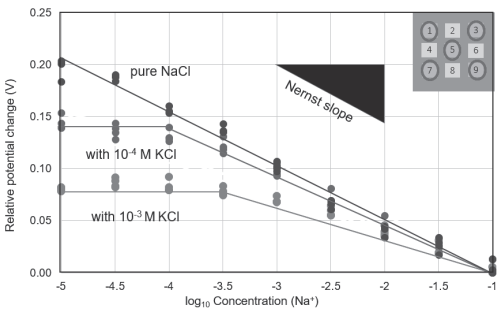

Figure 3: Calibration plot for the Na^+ ion-selective membranes.

Figure 2 shows the calibration plot for the K^+ ion-selective membrane. The linear range extended down to 10^{-5} mol/l KCl, with an average sensitivity of 61.7 mV/decade. With 10^{-3} mol/l Na^+ as interfering ion, the linear range was only down to $10^{-3.5}$ mol/l, below which the membrane was no more sensitive to KCl concentration.

Figure 3 shows the calibration plot for the Na^+ ion-selective membrane, the linear range extended down to 10^{-5} mol/l NaCl with an average sensitivity of 56.7 mV/decade. With 10^{-3} mol/l K^+ as interfering ion, the linear range was only down to $10^{-3.5}$ mol/l, below which the membrane was no more sensitive to NaCl concentration.

6. Conclusion

In this work, the surface of the insulating layer of the sensor chip has been modified with four K^+ ion-selective membrane and five Na^+ ion-selective membranes and measurements were carried out simultaneously. Sensitivity and cross-sensitivity under the existence of interfering ions were also characterized. Furthermore, a life time of the sensor over 3 weeks has been obtained.

References

1. Owicki, J. C. *et al.* The light-addressable potentiometric sensor: Principles and biological applications. *Annu. Rev. Biophys. Biomol. Struct.* **23**, 87–113 (1994).
2. Ermolenko, Y. *et al.* Photocurable membranes for ion-selective light-addressable potentiometric sensor. *Sensors Actuators, B Chem.* **85**, 79-85 (2002).